# Generation of metallosupramolecular polymer gels from multiply functionalized grid-type complexes

# Generation of metallosupramolecular polymers from multiply functionalized grid-type complexes

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*Received (), Accepted*
*DOI:*

**A ditopic ligand (1), containing two tridentate bis(acylhydrazone) subunits and bearing both long alkyl chains and hydrogen-bonding groups, has been synthesised. Metal cation binding in the presence of base leads to hierarchical self-assembly, forming first a neutral [2x2] grid-type complex (2) that organizes into metallosupramolecular polymer gels in toluene.**

## Introduction

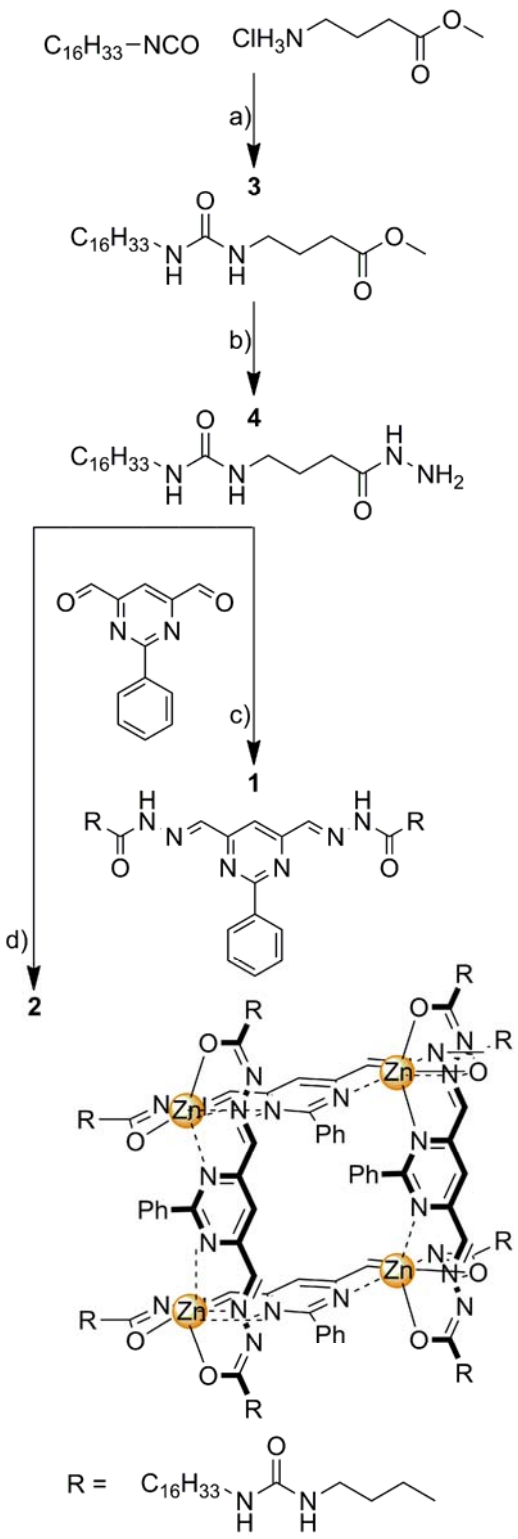
Nature employs a combination of supramolecular interactions (electrostatic, hydrophobic, π-π, van der Waals forces, hydrogen-bonding and metal coordination) in order to generate hierarchically ordered structures with remarkable properties, as diverse as those of high tensile strength, reaction catalysis or light-harvesting ability.[1] The same structure-directing forces can, in principle, be employed for the exploitation of a vast number of synthetic functional units in new materials of similar or perhaps greater utility.[2] Such units include oligonuclear metallosupramolecular architectures such as grids,[3] helicates[4] and racks[5] that are known to display interesting electronic, magnetic and optical properties. Suitable functionalization of such entities allows for further hierarchical assembly into self-organized arrays with emergence of novel properties. Solid state arrangements of specific [2x2] grid-type complexes have been obtained in this manner.[6] We now describe the design and behavior of modified metallogrid complexes suitable for the formation of functional organogels.

Gel formation by supramolecular polymers[7] is analogous to biopolymer gelation. The ångström to nanometer scale structure of supramolecular polymers is programmed by the chemical structure of the monomers. The nano- to micrometer structural domain is determined by the morphology of local segments of the polymers formed (e.g. coils, fibres, ribbons or sheets), and the interactions between individual polymer chains to give a non-crystalline, continuous but open network within which solvent may be included and indeed form an essential part. Supramolecular polymer gels have been the subject of great research interest both in order to elucidate their structures at different length scales, and to explore their promise in applications as diverse as tissue scaffolds for regenerative tissue engineering, hybrid materials[8] or novel electronic materials.[9]

Relatively few examples are known of supramolecular polymers incorporating metal complexes which form functional metallo-organogels. Triazole ligands bearing large lipophilic substituents are known to form coordination polymers with Fe(II) salts of long chain sulfonates that gelate solvents such as dodecane within which unusually subtle control of spin-crossover is possible.[10] Remarkable variations in the emission characteristics of Au(I) complexes of functionalised diazine ligands can be induced upon their incorporation into organogels.[11] Control of the emission characteristics of Cu(II), Pd(II) and Pt(II) complexes of 8-hydroxyquinoline ligands bearing lipophilic substituents has been achieved in a similar fashion.[12] Certain bis(bipyridyl)binaphthyl ligands[13] gelate organic solvents (and mixtures thereof)[14] due to the formation of helical polymeric Cu(I) complexes, and xerogels formed from such coordination polymers have been demonstrated to catalyze 1,3-dipolar Huisgen cycloaddition reactions in water.[14] Furthermore, films composed of dynamic metallosupramolecular polymers have been shown to be capable of undergoing remarkable changes in their mechanical and optical properties upon reshuffling of their components.[15]

Metallosupramolecular grid complexes (particularly [2x2] tetranuclear grids)[3] are known to exhibit potentially useful electronic,[16] magnetic[6,17] and optical properties.[18] With appropriate external functionalisation, it is possible to prepare grids that assemble into well-defined 1D- and 2D-architectures via metal ion coordination.[3,6] Further, the enhancement of ligand acidity resulting from metal ion coordination can allow such grids to be obtained in overall uncharged forms in principle suited to dispersion in non-polar media. Thus, we describe herein a system displaying three-step hierarchical self-assembly, first of two subunits into ligand **1**, then of **1** and metal cations into a neutral metallo-supramolecular grid complex **2**, that is thereafter capable of generating a 3D-architecture, macroscopically expressed in the formation of a supramolecular polymer organogel. This process is expected to be characteristic of a potentially large family of related species, differing in regard to the metal ion

incorporated within the grid complex as well as in the chains borne by the central core.




Scheme 1. Synthesis of the bis(acylhydrazone) (**1**) and [2x2] grid (**2**) studied herein: a) $Et_3N$, $CH_2Cl_2$, 40 °C, $N_2$ atmosphere, 18 h (77 %); b) hydrazine hydrate, EtOH, 80 oC, N2 atmosphere, 18 h (53 %); c) $CHCl_3$, MeOH, room temperature, $N_2$ atmosphere, 24 h (91 %); d) $ZnCl_2$, $Et_3N$, $CHCl_3$, MeOH, room temperature, $N_2$ atmosphere, 24 h (90 %).

## Results and Discussion

### Synthesis of ligand 1 and of its [2x2] grid complex 2

A particular advantage in the formation of grid complexes from bis(acylhydrazone) ligands[19] is that such ligands can be generated from carboxylic acid hydrazides, which are readily obtained from the corresponding esters, thereby allowing a wide variety of carboxylic acids to be exploited. To obtain a ligand containing both H-bonding and lipophilic moieties necessary for organogel formation, methyl 4-aminobutyrate was reacted with hexadecylisocyanate, yielding a urea-containing ester **3**, which was then treated with hydrazine at reflux in order to provide an acylhydrazine, **4**. Condensation of a twofold molar amount of this acylhydrazine with 2-phenylpyrimidine-4,6-dicarbaldehyde alone yielded the bis(acylhydrazone) ligand (**1**), while the same reaction in the presence of zinc chloride and triethylamine yielded a solid (**2**) with the bright yellow-orange colour typical[19] of a [2x2] $Zn_4$ grid-type structure, formed by ionization of the N-H site of the ligand in the complex (Scheme 1). Indeed, the MALDI-TOF MS spectrum of this material confirmed the presence of the tetranuclear species (see Fig. S1).

### Supramolecular self-assembly of ligand 1 and of its [2x2] grid complex 2

The behaviour of solutions of the bis(acylhydrazone) (**1**) and the [2x2] grid (**2**) was investigated in either pure chloroform or pure toluene. The bis(acylhydrazone) could be dissolved in hot chloroform at a concentration of 20 mg/ml, and after slowly cooling to room temperature the solution was clear and non-viscous. In contrast, after dissolution in hot toluene and cooling, it gave a somewhat cloudy, viscous solution due to the formation of fibrillar assemblies of supramolecular polymers[20] that were clearly observable by scanning electron microscopy (SEM) (see Fig. S2). The [2x2] grid was soluble in hot chloroform and toluene at a concentration of 20 mg/ml. Slow cooling of the chloroform solutions to room temperature resulted in somewhat cloudy and viscous solutions, whereas cooling the toluene solutions yielded slightly cloudy organogels composed of fibrillar networks of supramolecular polymers (see Fig. 1).

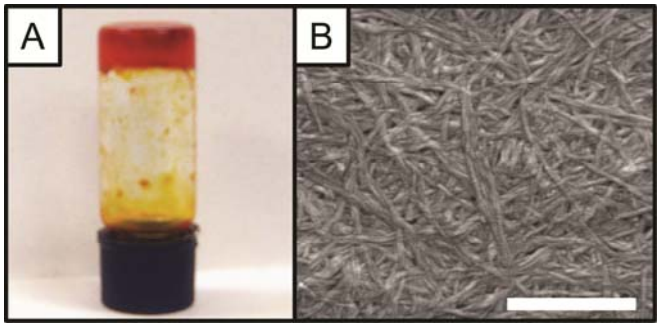



Figure 1. A) Photograph of a metallo-supramolecular polymer organogel formed by **2** at a concentration of 20 mg/ml in toluene. B) SEM image of a dried sample of the organogel formed by **2** at a concentration of 20 mg per mL in toluene (scale bar represents 1000 nm).

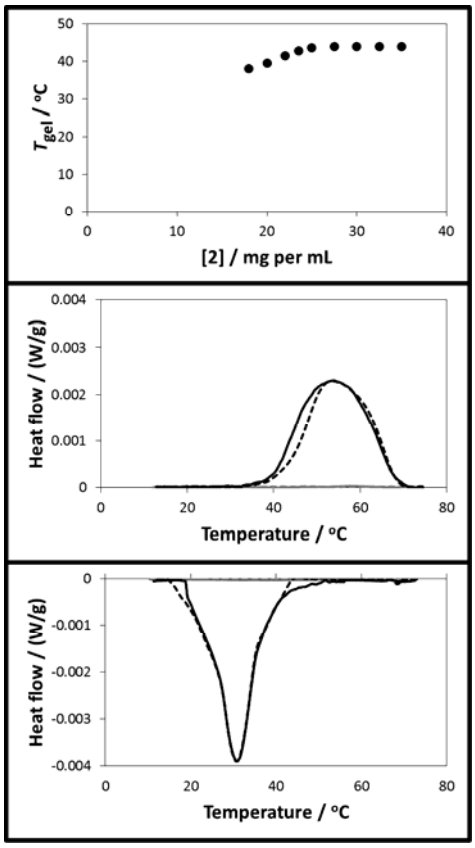



Figure 2. Top) Effect of concentration of 2 in toluene on the $T_{gel}$ value determined by the tube inversion method. Middle) DSC thermograms. Black lines are samples of **2** at a concentration of 20 mg/ml in toluene; 1st heating cycle (solid black line), 2nd heating cycle (dashed black line). Grey lines are pure toluene; 1st heating cycle (solid grey line), 2nd heating cycle (dashed grey line). Bottom) Black lines are samples of 2 at a concentration of 20 mg/ml in toluene; 1st cooling cycle (solid black line), 2nd cooling cycle (dashed black line). Grey lines are pure toluene; 1st cooling cycle (solid grey line), 2nd cooling cycle (dashed grey line).

The minimum concentration of gelator (MGC) required for **2** to induce gelation in toluene above room temperature was found to be 18 mg/ml. The thermal stability of the gels was studied by determining the $T_{gel}$ values (the temperature at which the gel becomes a sol) of samples of 2 at various concentrations in toluene via the tube inversion method (Fig. 2).[20] Increasing the concentration from 18 mg/ml to 25 mg/ml increased the $T_{gel}$ value from 38 to 44 °C, the $T_{gel}$ values being concentration independent between 25 mg/ml and 35 mg/ml (a concentration-independent or "plateau" region has been observed for related organogelator systems),[21] and more concentrated samples were not studied due to their inhomogeneity. Differential scanning calorimetry of samples of **2** at a concentration of 20 mg/ml revealed that the gel-sol transition occurred over a broad temperature range with an endothermic peak from 35 to 67 °C (Fig. 2), the onset of which corresponds to the $T_{gel}$ value determined by tube inversion. The broad exothermic peak between 48 and 18 °C observed on cooling demonstrated the full thermoreversibility of the self-assembly process (Fig. 2). Furthermore, rheological measurements on samples of **2** at a concentration of 20 mg/ml demonstrated that the samples were true gels since the storage modulus (G') was greater than the loss modulus (G''), and both are independent of frequency in the linear viscoelastic regime tested.[22] The storage modulus of the gels (ca. 120 Pa) was of a similar magnitude to that of other metallosupramolecular polymer organogels reported in the literature (Fig. 3).[22b,23]

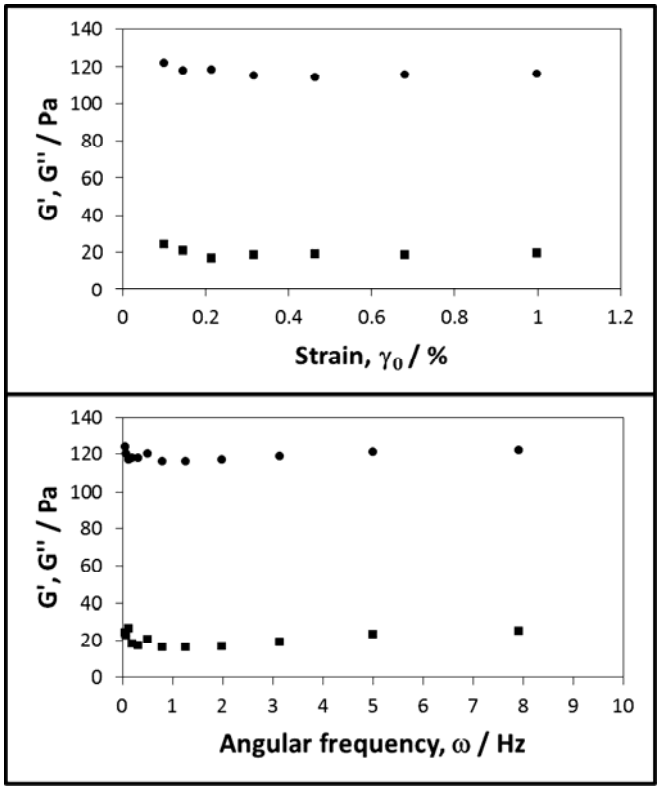



Figure 3. Top) Stress sweep of **2** at a concentration of 20 mg/ml in toluene. Bottom) Oscillatory frequency sweep of 2 at a concentration of 20 mg/ml in toluene.

**Proton NMR spectroscopic investigations of the organogel formed by 2**

Independent indications of association in solution were obtained by $^1$H NMR spectroscopy. At room temperature, all signals of **1** and **2** at a concentration as low as 2 mg/ml in toluene were broad, consistent with the formation of supramolecular polymers. This broadening was such as to render recording of a room temperature spectrum difficult, and the peak intensities were not markedly enhanced by heating the samples to 85 °C (Figs. S3 and S4). Studies carried out in chloroform were more informative due to the lower degree of association. $^1$H NMR signals for solutions of **1** at a concentration of 2 mg/ml were sharp at room temperature, indicative of no (or very low levels of) association (Fig. S5). In contrast, the spectral peaks for samples of **2** at a concentration of 2 mg/ml were broad at room temperature but became sharper at higher temperatures (Fig. S6). The signals due to the protons of the urea moieties were observed to undergo upfield shifts at elevated temperatures (from ca. 5.25 ppm at 25 °C, to 5.08 ppm at 55 °C), indicative of the disruption of the hydrogen-bond mediated assemblies.[24] Furthermore, signals of more concentrated samples of **2** (10 mg/ml) were much broader, consistent with the decreased mobility of the grid complexes due to a greater degree of association resulting from a multivalent promotion of array formation (Fig. 4).

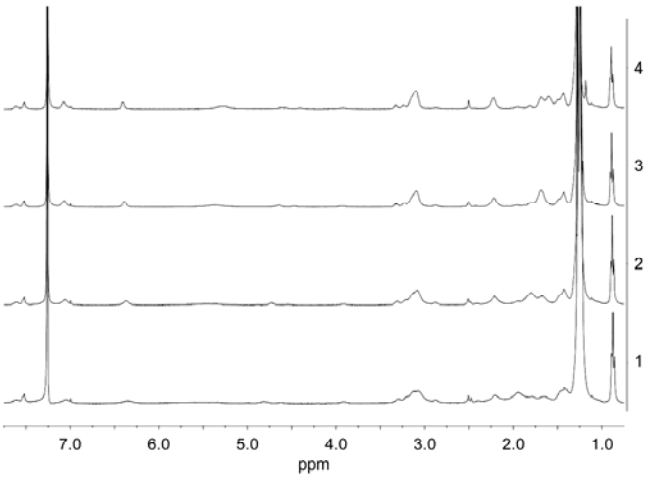



Figure 4. NMR spectra of **2** at a concentration of 10 mg/ml in $CDCl_3$ at: 1) 25 °C, 2) 35 °C, 3) 45 °C, 4) 55 °C.

**IR spectroscopic investigations of the organogel formed by 2**

Fourier Transform Infrared (FTIR) absorption spectroscopy was also used to characterize the association of **1** and **2** at various concentrations in chloroform and toluene at room temperature. Urea moieties have three characteristic absorption bands: the N-H stretch ($\nu_{NH}$, typically between 3450 $cm^{-1}$ 'free' in solution, and 3300 $cm^{-1}$ strongly hydrogen bonded); the C=O stretch, known as the amide I band ($\nu_{CO}$, typically between 1695 and 1620 $cm^{-1}$); and a band corresponding to a combination of the N-H deformation and the C-N stretch, known as the amide II band ($\delta_{NH}$ and $\nu_{CN}$, typically between 1590 and 1550 $cm^{-1}$). There are two potential structures for urea-urea hydrogen bonding: in the first, each carbonyl oxygen forms two hydrogen bonds to two hydrogen atoms (amide II band maxima at ca. 1580 $cm^{-1}$); whereas in the second, the carbonyl oxygen forms a single slightly stronger hydrogen bond to a hydrogen atom (amide II band maxima at ca. 1575 $cm^{-1}$).[25]

A 10 mg/ml solution of **1** in chloroform showed absorption corresponding to an urea N-H stretch at 3343 $cm^{-1}$, whereas in toluene it was shifted to 3339 $cm^{-1}$, indicating a greater degree of intermolecular hydrogen bonding in toluene, as expected due to the fact that chloroform is a hydrogen bond donor (Table 1, Fig. S7). The amide I and II bands were observed to shift from 1623 and 1572 $cm^{-1}$ to 1625 and 1574 $cm^{-1}$ respectively. The changes, though minor, are consistent with the carbonyl oxygen of the urea moieties forming a single hydrogen bond to a hydrogen atom on another urea in chloroform, whereas in toluene it forms two hydrogen bonds to two hydrogen atoms on another urea (Table 1, Fig. S8). This arrangement of hydrogen bonds was also observed to be preferred in analogous bisureas forming supramolecular polymer organogels.[25b,c] The absorption maxima characteristic of the antisymmetric ($\nu_{as}$) and symmetric ($\nu_s$) stretches of the $CH_2$ group of the alkyl chains occurred at 2918 and 2849 $cm^{-1}$ respectively, in both chloroform and toluene, which is indicative of tightly packed chains.[26] The absorption peaks at ca. 1467 and ca. 1457 $cm^{-1}$, and absence of absorption at 1460 $cm^{-1}$ or between 1370 and 1340 $cm^{-1}$ suggests that the chains are highly ordered (Table 1, Figs. S9, S10).

The IR spectra of grid (**2**) at a concentration of 10 mg/ml in chloroform and toluene were almost identical. The position of the amide I and II bands of the ureas at 1626 and 1574 $cm^{-1}$ respectively (Fig. S11), showed that the carbonyl oxygen of the urea moieties formed two hydrogen bonds to two hydrogen atoms on another urea moiety in both chloroform and toluene (in contrast to assemblies of **1** which were more affected by the hydrogen-bond donating chloroform). Interestingly, the absorption maximum corresponding to the urea N-H stretch of **2** at 3332 $cm^{-1}$ (Table 1, Fig. S12), was strongly shifted from the corresponding absorption peak of **1** in both chloroform and toluene, supporting the NMR data indicating that urea-mediated hydrogen-bonding interactions play an important role in the assembly of the grid complexes into supramolecular polymer organogels. The absorption bands characteristic of the antisymmetric ($\nu_{as}$) and symmetric ($\nu_s$) stretches of the $CH_2$ groups of the alkyl chains of 2 at 2919 and 2850 $cm^{-1}$ are indicative of tightly packed chains (Table 1, Fig. S12), although their small shift from the corresponding bands for **1** points to a little more chain fluidity. The bands at 1467 and 1457 $cm^{-1}$ and absence of absorption between 1370 and 1340 $cm^{-1}$ clearly show that the alkyl chains in assemblies of **2** are highly ordered in analogy to assemblies of **1** (Table 1, Figs. S13, S14).

Table 1. A summary of the relevant peaks in the FTIR absorption spectra of **1** and **2** at a concentration of 10 mg/ml in chloroform (Ch) and toluene (Tol).

| System | Wavenumber / $cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | NH | $\nu_{as}$ $CH_2$ | $\nu_s$ $CH_2$ | Amide I | Amide II | $\nu_s$ $CH_3$ |
| **1** in Ch | 3343 | 2918 | 2849 | 1623 | 1572 | 1374 |
| **1** in Tol | 3339 | 2918 | 2849 | 1625 | 1574 | 1374 |
| **2** in Ch | 3332 | 2919 | 2850 | 1626 | 1574 | 1372 |
| **2** in Tol | 3332 | 3332 | 2850 | 1626 | 1574 | 1372 |

**Conclusions**

The results described here show that an appropriately functionalised neutral metallogrid complex can be used to obtain organogels in which the grid species is intact. The incorporation of urea moieties results in H-bonding interactions that are important in generating supramolecular polymers that gelate toluene. While the present work has been focused solely on a Zn(II) grid, given the ready formation of grids by similar ligands with numerous metal ions, it is anticipated that organogels expressing the properties of a wide variety of metal ions should be readily accessible. In particular, the corresponding gels formed from Co(II) and Fe(II) [2x2] grids may present interesting optical, electronic and magnetic properties.[3,5,16] It is worth stressing three main features of the present systems:

1. The easy accessibility of bis(acylhydrazone) ligands similar to **1**, bearing a large variety of functionalized side-chains.
2. The generation of neutral polynuclear metalloarrays by ionization of the N-H sites of the acylhydrazone group,

yielding organosoluble entities, unperturbed by counterions.
3. The multivalency generation, from monovalent to octavalent, via the one-pot hierarchical assembly of two subunits, a monovalent acylhydrazine component and a dialdehyde, and metal ions (in presence of a base) into the functionalized grid architecture 2, which allows for multiple supramolecular interactions and network self-organization.

## Experimental Section

### Materials and Methods

Reagents were obtained from Sigma-Aldrich and used without further purification unless otherwise noted. 2-phenylpyrimidine-4,6-dicarbaldehyde was prepared as previously described.[19] Mass spectrometry (electrospray (ES-MS) and MALDI-TOF-MS) was performed by Dr. Xianwen Lou in the Laboratory of Macromolecular and Organic Chemistry, at the Eindhoven University of Technology. $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker Ultrashield Avance 400 instrument, using residual solvent proton resonances as internal references for the $^{1}$H NMR spectra and the solvent $^{13}$C peaks as references for the $^{13}$C NMR spectra. The following notation is used for the 1H NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m), broad (br). UV-visible absorption spectra were recorded at room temperature on a Beckman Coulter DU720 general purpose UV-visible spectrophotometer using a quartz cuvette with a pathlength of 1 mm.

### Synthesis and characterisation

**Ester precursor** (**3**): Hexadecylisocyanate (1.72 g, 6.42 mmol), methyl 4-aminobutyrate hydrochloride (0.735 g, 4.78 mmol) and triethylamine (2.02 g, 19.93 mmol) were added to dichloromethane (10 mL). The mixture was heated at reflux under nitrogen for 18 hours, after which the volatiles were removed via rotary evaporation. The residue was dissolved in ethanol to which the addition of several drops of water gave a cloudy solution, which was left to recrystallize at 4 °C for 16 h. The precipitate was isolated via filtration, washed with small portion of cold ethanol, and dried under high vacuum, yielding the product as a white solid **3** (1.42 g, 3.69 mmol, 77 %). High resolution ES-MS: m/z(%) = 385.2500 (100) $[M+H]^+$, 407.3333 (100) $[M+H]^+$. $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.60 (br, 2 H); 3.68 (s, 3 H); 3.22 (t, 3J = 6.8 Hz, 2 H); 3.15 (t, $^{3}J$ = 6.8 Hz, 2 H); 2.39 (t, $^{3}J$ = 6.8 Hz, 2 H); 1.84 (m, 2 H); 1.50 (m, 2 H); 1.26 (m, 26 H); 0.88 (t, $^{3}J$ = 6.8 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) = 174.15; 158.17; 51.69; 40.71; 39.93; 31.91; 31.29; 30.16; 29.68; 29.65; 29.59; 29.57; 29.35; 26.89; 25.29; 22.68; 14.11.

**Acylhydrazine precursor** (**4**): To a stirred solution of ester precursor **3** (1.95 g, 5.0 mmol) in 40 mL ethanol was added excess hydrazine hydrate and the mixture was heated at reflux under nitrogen for 18 hours, after which it was allowed to cool to room temperature. The precipitate was isolated via filtration and dried under high vacuum, yielding the product as a white solid **4** (1.03 g, 2.68 mmol, 53 %). High resolution ES MS: m/z(%) = 385.2500 (100) $[M+H]^+$. $^{1}$H NMR (400 MHz, CDCl3:TFA 1:1): δ (ppm) = 3.35 (t, 3J = 6.6 Hz, 2H), 3.22 (t, $^{3}J$ = 7.4 Hz, 2H), 2.56 (t, $^{3}J$ = 6.8 Hz, 2H), 1.99 (d, $^{3}J$ = 6.7 Hz, 2H), 1.58 (m, 2H), 1.38 – 1.16 (m, 30H), 0.87 (t, $^{3}J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$:TFA 1:1): δ (ppm) = 174.35, 159.66, 42.44, 40.69, 32.23, 30.13, 29.99, 29.98, 29.97, 29.95, 29.94, 29.88, 29.79, 29.66, 29.29, 28.89, 26.75, 23.94, 22.95, 14.16.

**Bis(acylhydrazone) ligand** (**1**): The compound was prepared in accordance with the literature precedent.[19] Briefly, 2-phenylpyrimidine-4,6-dicarbaldehyde (0.112 g, 0.53 mmol) and acylhydrazine precursor (0.429 g, 1.12 mmol) were stirred in a solution of chloroform (5 mL) and methanol (5 mL) under nitrogen for 24 h at room temperature, after which the volatiles were removed via rotary evaporation. The residue was washed with acetonitrile to remove unreacted starting material, and the resultant solid dried under vacuum, yielding a white solid **1** (0.456 g, 0.48 mmol, 91 %). High resolution ES-MS: m/z(%) = 945.9167 (100) $[M+H]^+$. $^{1}$H NMR (400 MHz, $CDCl_3$:TFA 1:1): δ (ppm) = 8.67, 8.57, 8.44, 8.34, 8.30, 8.28, 8.23, 7.86, 7.73, 7.71, 7.69, 3.44, 3.32, 3.30, 3.28, 3.26, 3.08, 3.07, 2.71, 2.69, 2.68, 2.66, 2.12, 2.11, 1.64, 1.62, 1.31, 1.28, 0.88, 0.86. $^{13}$C NMR (100 MHz, $CDCl_3$:TFA 1:1): δ (ppm) = 174.33, 159.15, 139.27, 130.02, 129.12, 116.01, 114.99, 113.17, 112.10, 42.09, 40.53, 31.76, 29.52, 29.48, 29.42, 29.34, 29.22, 29.19, 28.85, 28.45, 26.30, 22.43, 13.41, 5.81.

**[2x2] grid complex** (**2**): The compound was prepared in accordance with the literature precedent.[20] Briefly, 2-phenylpyrimidine-4,6-dicarbaldehyde (0.112 g, 0.53 mmol), 1 (0.429 g, 1.12 mmol), $ZnCl_2$ (0.072 g, 0.53 mmol) and triethylamine (0.5 mL, excess) were stirred in a solution of chloroform (8 mL) and methanol (2 mL) under nitrogen for 24 hours at room temperature, after which the volatiles were removed via rotary evaporation. The residue was washed with acetonitrile to remove triethylammonium hydrochloride and any unreacted starting materials, and the resultant product dried under high vacuum, yielding a bright orange solid, **2** (0.487 g, 0.12 mmol, 90 %). MALDI-TOF-MS: m/z(%) = 4037.24 (100) $[M+H]^+$ (see Fig. S1 top). The UV-visible spectra in chloroform and toluene are given in the supplementary information (see Fig. S1 bottom).

**Preparation of Organogels**: An accurately measured mass of gelator **2** was weighed out into a 2 mL glass vial with an internal diameter of 5 mm, to which the solvent (0.5 mL) was added, and the vial was fitted with an air-tight seal. Samples were sonicated at 40 °C for 60 min, followed by heating in an oil bath until a homogeneous solution was obtained, and subsequently allowed to cool to room temperature. The samples were left to stand overnight. Gelation was considered to have occurred when a homogeneous 'solid-like' material was obtained that exhibited no gravitational flow.

**Determination of $T_{gel}$ values**: The thermally reversible gel–sol transition temperature ($T_{gel}$) was determined by placing the glass vial containing the gel into a high precision oil bath, and increasing the temperature of the oil in the bath at a rate of 0.5 °C per minute. The temperature at which solvent began to run from the gel was recorded as the $T_{gel}$ value.[21]

**Differential Scanning Calorimetry**: Differential scanning calorimetry (DSC) experiments were carried out with a TA Instruments DSC 2920 (calibrated with a sapphire standard), using airtight aluminium pans sealed under a nitrogen atmosphere. The heating rate was 0.5 °C per minute.

**Infrared spectroscopy**: Fourier transform infrared (FTIR) spectra of the organogels were recorded on a

Bruker Tensor 27 FTIR spectrometer. Spectra of all gels were recorded in absorbance mode at 21 °C, with a 1 $cm^{-1}$ resolution and 60 scans (corrected for background and atmosphere using OPUS software). A spectroscopic cell with NaCl windows separated by 1 mm was used for the measurements.

**Rheological characterization**: An Anton Paar Physica MCR101 rheometer using a cone and plate geometry was utilized. The gap distance between the cone and plate was typically 1 mm. Stress amplitude sweep experiments were performed at a constant oscillation frequency of 1.6 Hz at a temperature of 25 °C. Oscillatory frequency sweep experiments were performed in the linear viscoelastic region (at a strain of 0.2 %) to ensure that calculated parameters correspond to an intact network structure. The rheometer was connected to a computer running Rheoplus software which converts the torque measurements into the storage modulus (G') and the loss modulus (G'') in oscillatory shear experiments. Solvent evaporation was minimized by conducting the experiment in an atmosphere saturated with solvent.

**Scanning Electron Microscopy**: A small amount of gel sample was removed from its glass vial with a spatula, placed onto a metal stub and left to dry overnight in a fume hood. The sample was covered in a thin layer (4 nm) of Ir using a Cressington 208 benchtop sputter coater before being observed with a Zeiss Supra 40 VP Scanning Electron Microscope (SEM) operating at 3 kV.

Supporting Information (see footnote on the first page of this article): MALDI-TOF, UV-visible, SEM, NMR and FTIR referred to in the text.


**Acknowledgments**

J. G. H. gratefully acknowledges the financial support of an Entente Cordiale Scholarship. We gratefully acknowledge Dr. Xianwen Lou of the Laboratory of Macromolecular and Organic Chemistry at the Eindhoven University of Technology for carrying out mass spectrometry.


**Notes and References**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*Electronic Supplementary Material (ESI) available – Figures S1 – S14 : Mass, NMR, FTIR and UV-visible spectra of the ligand and grid and their gels ; SEM image of a dried toluene gel.*


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